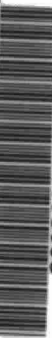


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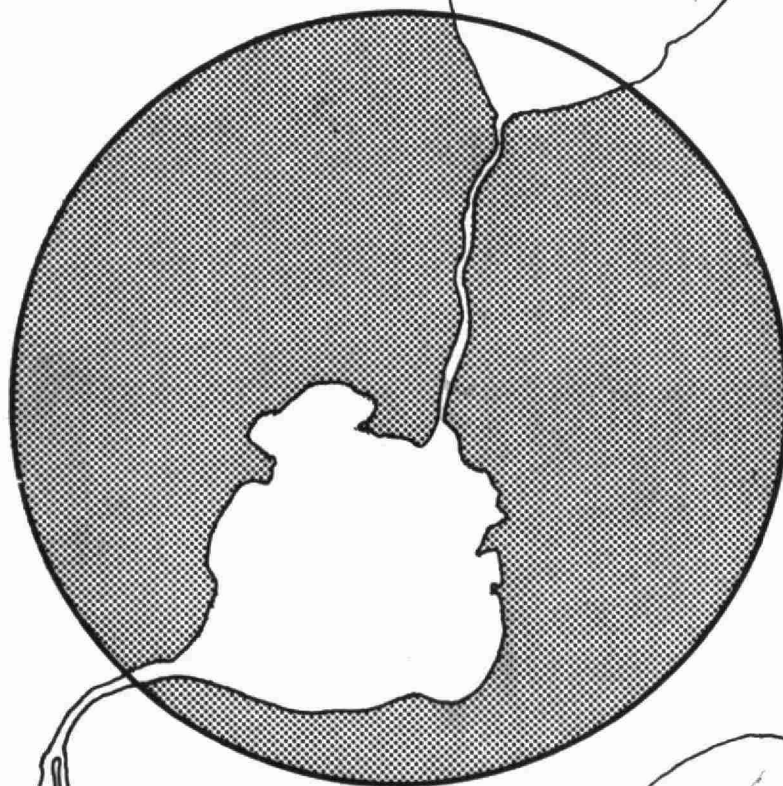
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report on the mercury pollution of the st. clair river system

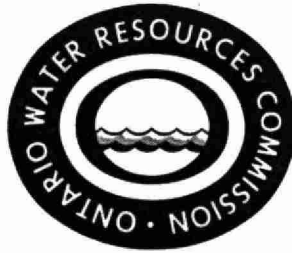
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ONTARIO WATER RESOURCES COMMISSION

REPORT ON
THE MERCURY POLLUTION
OF THE
ST. CLAIR RIVER SYSTEM

June, 1970

TABLE OF CONTENTS

	<u>PAGE NO.</u>
INTRODUCTION	1
1.1 SUMMARY	2
1.2 CONCLUSIONS AND RECOMMENDATIONS	3
2.1 HISTORY OF MERCURY CONTAMINATION	5
2.2 MERCURY AS A POLLUTANT	7
2.3 SOURCES OF MERCURY	9
2.4 MERCURY LOSSES FROM THE DOW CHLOR-ALKALI PLANTS AT SARNIA PRIOR TO APRIL 1970	12
2.5 REMEDIAL ACTION TAKEN AT THE DOW CHLOR-ALKALI PLANTS	15
2.6 EFFECT OF MERCURY	
(1) Concentrations in Fish	17
(2) Concentrations in Water	17
(3) Distribution in Sediments	17
2.7 STATUS OF COMMERCIAL AND SPORT FISHERY	
(1) Restrictions	20
(2) Loans	21
2.8 FUTURE COURSE OF ACTION AND ALTERNATIVES	23
(1) Take No Action	23
(2) Chemical Conversion of the Mercury	25
(3) Cover the Mercury-Laden Sediments	27
(4) Remove Mercury Contaminated Sediments	28
APPENDIX I	
MERCURY LOSSES TO THE ST. CLAIR RIVER FROM DOW CHEMICAL OF CANADA LIMITED (Sarnia)	34

	<u>PAGE NO.</u>
APPENDIX 2	
SUMMARY OF MERCURY ANALYSIS FOR ST. CLAIR RIVER AND LAKE ST. CLAIR	42
APPENDIX 3	
ANALYTICAL METHODS FOR MERCURY DETER- MINATION	54
BIBLIOGRAPHY	57

LIST OF TABLES

<u>TABLE NO.</u>		<u>PAGE NO.</u>
Appendix 2 1	Summary of Mercury Analysis on Fish Collected from Southern Lake Huron, St. Clair River, Lake St. Clair, Detroit River and Lake Erie (Erieau to Detroit River).	47

LIST OF FIGURES

<u>FIGURE NO.</u>		
1	St. Clair River Showing Mercury Concentrations in Sediments	19
2	Quantitative Recovery of Mercury by Dredging Sediments in the St. Clair River between Dow Complex and Bowens Creek	29
3	St. Clair River Zones of High Mercury Concentration	31
Appendix 1 1	Dow (Sarnia) Mercury Cell Operation	35
2	Dow (Sarnia) Average Daily Mercury Loss to Sewer by Year	36
Appendix 2 1	Mercury Content in Sediment Cores taken at Three Locations in the Vicinity of the Dow (Sarnia) Plant	46

LIST OF CHARTS

<u>CHART NO.</u>		<u>PAGE NO.</u>
Appendix 2		
1	St. Clair River Showing Mercury Sediment Samples	50
2	St. Clair River Showing Mercury Sediment Samples	51
3	St. Clair River Showing Mercury Sediment Samples	52
4	Lake St. Clair Showing Mercury Sediment Samples	53

INTRODUCTION

The potential environmental effects of mercury losses to the St. Clair River system from the Dow Chemical Canada Limited (Dow) complex in Sarnia were first brought to the attention of the Ontario Water Resources Commission (OWRC) early in 1969. The discovery of high mercury levels in fish in the St. Clair River and Lake St. Clair precipitated the closure in April of these waters to sport and commercial fishing. The extent of damages from the mercury pollution has been so severe that the government has found it necessary to make available to commercial fishermen and tourist camp operators interest free demand notes to assist in offsetting their loss of revenue. In May, the province lifted the ban on sport fishing in the St. Clair system.

This report summarizes the sources, nature and known effects of mercury losses to the St. Clair River and the remedial action taken to date; outlines the conclusions to be drawn from present investigations; and recommends a future course of action to reduce the existing mercury pollution. Emphasis is given to the practicability of removing mercury-laden sediments from the St. Clair River.

1.1 SUMMARY

Mercury lost from the Dow Chemical Company of Canada chlor-alkali complex at Sarnia has contaminated the bottom sediments of the St. Clair River and Lake St. Clair. This mercury has entered the aquatic food chain with the subsequent concentration of mercury in the flesh of fish.

Dow estimates that they have lost an average of thirty pounds per day to the St. Clair River over the last twenty years. In response to a Commission Order, Dow has reduced mercury losses to less than one pound per day through the installation of new facilities and the modification of operating procedures.

Government is making available interest free demand loans to assist commercial fishermen and tourist camp operators who have suffered damages by the closure of commercial fishing and the limiting of sport fishing in the area.

The possible future actions to alleviate the problems created by the mercury pollution are considered. The removal of contaminated sediments by dredging is the most suitable alternative for reducing mercury pollution in the St. Clair River.

1.2 CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Mercury pollution has caused severe damage to the commercial and sport fisheries and associated industries of the St. Clair River - Lake St. Clair system. The effects of pollution of the river sediments are expected to continue to influence the downstream waters for many years.
2. The damage has been sufficiently great that the Ontario government has seen fit to make available interest free demand loans to commercial fishermen and tourist resort operators.
3. To lessen the potential for the continued pollution of the Lower St. Clair River and Lake St. Clair by the mercury presently confined to the twelve mile section of the river below Dow, it would seem to be prudent to remove, by dredging, the polluted sediments from this reach of the river to the greatest extent possible. Dredging should be undertaken providing that the activity associated with dredging does not add to the problem.

RECOMMENDATION

The OWRC with the assistance of the Canada Department of Public Works should undertake a trial dredging experiment of a specified section of the St. Clair River at the expense of the Dow Chemical Company.

2.1 HISTORY OF MERCURY CONTAMINATION

Several incidents involving mercury contamination have been documented. Severe neurological disorders and the deaths of 41 persons in the vicinity of Minamata Bay in Japan during the period 1953 to 1960 were subsequently ascribed to the consumption of fish and shellfish contaminated with mercury discharged from a nearby organic chemical plant. A second poisoning incident occurred in Japan at Niigata in 1965 involving 26 cases, of which 5 deaths were reported.

In Sweden, the decline in seed-eating birds and their predators after the introduction of methyl mercury seed dressings in the 1940's forced the restriction in 1964 and the eventual banning in 1966 of the agricultural use of alkyl mercury compounds.

The occurrence of high levels of mercury in fish caused Swedish authorities to require that mercury in industrial effluents, principally from pulp and paper mills and caustic-chlorine plants, be severely restricted. The significance of metallic mercury losses from the caustic-chlorine (chlor-alkali) plants was not apparent to Swedish authorities until the high levels of mercury in fish were noted. The consumption of fish from certain Swedish waters was prohibited and fish containing more than 1 ppm of mercury were declared unfit for human consumption.

The Province of Alberta banned the hunting of pheasants and Hungarian partridges in 1969 because mercury concentrations in these birds were found to be in excess of 0.05 ppm (a Committee of the World Health Organization has recommended 0.05 ppm of mercury as the maximum permissible concentration for human consumption). These birds had apparently consumed seed grain treated with mercurial fungicides.

The Canada Department of Fisheries impounded fish from the Lake St. Clair fishery on March 24, 1970 after a number of fish collected by the Ontario Water Resources Commission and the Canadian Wildlife Service, were found to have a mercury content in excess of 0.5 ppm (the Federal Food and Drug Directorate tolerance level for commercial fish intended for human consumption).

2.2 MERCURY AS A POLLUTANT

All forms of mercury are toxic to man with the organic mercury compounds such as methyl mercury being more toxic than the inorganic compounds.

Mercury finds its way into the water in the form of metallic, inorganic divalent and phenyl mercury (Jernelov, 1969). While the latter two forms of mercury are readily available to the aquatic biota, metallic mercury is not. For this reason, it was once thought that metallic mercury could not enter the aquatic food chain. This supposition has since been discredited by the Swedish researchers Widmark, Jernelov, Jensen and Wood (Jensen, 1969 and Wood, 1968) who showed that metallic mercury could be transformed by micro-organisms (bacteriologically) to methyl mercury, mercuric salts and other organomercurials.

Upon discharge to the aquatic environment, metallic mercury accumulates in bottom muds. As previously discussed, microbiological activity in the sediments gradually converts metallic mercury to water-soluble methyl mercury in which form it can enter the food chain. Although some Swedish work has indicated that the principal mode of accumulation in fish is through the food chain (Jernelov, 1969), other workers have demonstrated that substantial absorption of methyl mercury occurs directly through the outer skin tissue, particularly the

gills (Jernelov, 1969 and Hannaerz, 1968). Both pathways exist, although the relative importance of each likely depends upon several variables such as the metabolic rate and feeding habits of fish involved, the time of year and the physical and chemical characteristics of the river or lake in question.

Elimination of mercury from fish tissue is a much slower process than its accumulation. Although it is impossible to estimate an accurate elimination rate owing to significant individual variation, Hannaerz (1968) estimated a biological half-life of mercury in muscles of pike of approximately 65-70 days, (these fish had been transferred to uncontaminated water). Johnels (in a field study), found no decrease in mercury levels in pike flesh a year after the source of contamination was eliminated. He concluded that mercury was still being liberated from bottom sediments. Predictions have been made that present mercury pollution of watercourses in Sweden may last for 10-100 years unless the mercury is physically removed from the watercourses, or isolated from the biota.

2.3 SOURCES OF MERCURY

Metallic mercury and compounds of mercury have numerous uses. In Ontario, the major use of mercury is as an electrode in the production of chlorine and caustic soda in chlor-alkali plants. Mercury is also used in the production of batteries and switch gear in the electrical industry, as a slimicide in the pulp and paper industry, as a catalyst in certain chemical reactions and in the production of fungicides, agricultural sprays, seed dressings, paints and pharmaceutical and dental preparations.

The loss of mercury from chlor-alkali plants and the loss of mercurial compounds used as fungicides and slimicides in the pulp and paper industry account for the major portion of the mercury which gains access to Ontario's lakes and rivers. Mercury losses from agricultural uses could also be significant.

In the St. Clair River area a number of potential sources exist from which mercury contamination could occur. They are:

- (1) the chlor-alkali plants of Dow Chemical of Canada Limited;
- (2) agricultural run-off;
- (3) run-off from golf courses and private homes using mercurial lawn fungicides and tree sprays;
- (4) sewage treatment plant effluents;

- (5) atmospheric fall-out from fossil fueled generating stations and foundries.

Mercury losses from the Dow chlor-alkali plants at Sarnia have been assessed. The other potential sources mentioned probably contribute to the background levels of mercury normally encountered.

Maintenance dredging of the navigation channels of the St. Clair River could be a factor in the distribution of mercury pollution. Each year, dredging is carried out in the St. Clair River, in the St. Clair cutoff and in Lake St. Clair. The volume of materials dredged from these areas is usually between 80,000 and 190,000 cubic yards annually. This material could increase mercury pollution in the spoil disposal areas of Lake St. Clair and Lake Huron if taken from areas where mercury residuals in the sediments are significant.

Following the disclosure of mercury losses from the Dow Chemical complex, the U. S. Federal Water Quality Administration (FWQA) and the Michigan Water Resources Commission (MWRC) undertook a study of the Lower St. Clair River - Lake St. Clair - Detroit River - Western Lake Erie area. They found that the Wyandotte Chemicals Corporation South Works chlor-alkali plant at Wyandotte, Michigan was consuming 80 pounds per day of mercury of which 10 to 20 pounds per day was entering the Detroit River. As of April 26, 1970, the Wyandotte Chemicals Corp. ceased discharging mercury to the Detroit River.

The FWQA and the Ohio Department of Health undertook a study of the Ohio section of Lake Erie. They found that the DetriX Chemical Corporation chlor-alkali plant at Ashtabula, Ohio was consuming 760 pounds of mercury per month. Analysis of samples of wastewater from the DetriX Corp. indicate that approximately 20 pounds per day of mercury was discharged in the effluent from the plant. On April 13, 1970, the Ohio Water Pollution Control Board issued an order to DetriX Chemical Corp. to eliminate any discharge of mercury in their effluent. On April 17, 1970, DetriX Chemical Company announced that they had stopped the loss of mercury from their plant.

In the St. Clair River - Lake St. Clair - Detroit River - Western Lake Erie system, the three chlor-alkali plants located at Sarnia, Ontario, Wyandotte, Michigan and Ashtabula, Ohio were each discharging significant amounts of mercury to the aquatic environment. At present, all three plants have taken the necessary steps to prevent the loss of mercury in their effluents.

2.4 MERCURY LOSSES FROM THE DOW CHLOR-ALKALI PLANTS AT SARNIA PRIOR TO APRIL 1970

The manufacture of chlorine and caustic soda from brine is a simple electrolytic process in which chlorine gas is liberated at the anode and sodium ions at the cathode.

There are three chlor-alkali plants in the Dow complex at Sarnia utilizing solution-mined underground salt as raw material. Two of these plants use carbon and mercury electrodes while the third uses carbon and steel electrodes separated by an asbestos diaphragm.

The first mercury cell chlor-alkali plant was put into operation at Dow in 1949. In the mercury cell, brine is recirculated countercurrent to the mercury cathode. There is a continuous make-up of strong brine solution from the salt cavern while lean brine is returned to the cavern.

In the electrolytic process the cathode mercury forms an amalgam with sodium. This amalgam is then reacted with water to produce caustic soda solution, free mercury and hydrogen gas. Some of the mercury is vaporized by the heat generated during the destruction of the amalgam and the production of hydrogen gas. Direct contact spray coolers were formerly used to cool the hydrogen and condense the mercury prior to venting the hydrogen to the atmosphere. The coolers produced a liquid effluent which, depending upon the efficiency

and maintenance of small interceptor devices, contained significant amounts of metallic mercury. The replacements of these spray coolers by more efficient indirect coolers and the recycle of the mercury condensate to the cell has been the major factor in reducing metallic mercury losses from this plant (see Appendix 1, Figure 1, Dow (Sarnia) Mercury Cell Operation).

Metallic mercury and salts of mercury are picked up in the mercury cell and are discharged to the salt caverns in the lean brine solution. Periodic losses of brine which occurred during plant shutdowns or maintenance resulted in the loss of mercury to the river.

The diaphragm (non-mercury) cell utilizes the same brine feed as the mercury cells. Effluent from this cell contained mercury because of the contamination of the brine feed by losses from the mercury cells to the salt caverns. In the case of the diaphragm cell impurities such as calcium and magnesium salts must be chemically precipitated and removed by sedimentation before the brine is directed to the cell. Brine sludge from this process was disposed at a company land fill site which is located in the drainage basin of Talford Creek. Run-off from this area may be the cause of the significant mercury contamination of bottom sediments in Talford Creek and in the St. Clair River in the vicinity of the mouth of Talford Creek.

The precise history of mercury losses from the Dow complex

since the beginning of the chlor-alkali plant operation in 1949 is obscure. In a letter dated February 27, 1970, the company reported that mercury losses to the St. Clair River from the two mercury cell chlor-alkali plants for the period July 1969 to February 1970 averaged 75 pounds per day, ranging from 195 pounds per day to 47 pounds per day. The company deny reports that over the 20 year period, losses have averaged 200 pounds per day. Their own estimates put the loss at an average of no more than 30 pounds per day for the 20 year period. This loss was largely as metallic mercury (see Appendix 1, Figure 2 - Dow (Sarnia) Average Daily Mercury Loss to Sewer). Summaries of the daily mercury losses from the Dow chlor-alkali plants from April 9, 1970 to May 30, 1970 as reported by Dow, are included in Appendix 1.

2.5 REMEDIAL ACTION TAKEN AT THE DOW
CHLOR-ALKALI PLANTS

On March 26, 1970, Dow was issued a Requirement and Direction under Section 50 of the Ontario Water Resources Commission Act, the main points of the Requirement being as follows:

- (i) Commencing April 15 to submit reports every fifteen days on the flow and mercury content of all effluent streams.
- (ii) To install treatment facilities or other measures on or before May 1, or a later date if application is made before April 24, to eliminate mercury losses in the following areas:
 - (1) hydrogen coolers,
 - (2) recirculating brine system,
 - (3) floor drainage,
 - (4) brine treatment sludges,
 - (5) chlorine drying agent.
- (iii) To maintain all such facilities in operating condition.

The procedures that were proposed to comply with the OWRC requirement can be briefly summarized as follows:

- (1) The installation of indirect hydrogen coolers and the recycle of the mercury condensate to the cell;
- (2) The installation of emergency holding facilities for excess brine and the discontinuance of sewerage brine.
- (3) The installation of corrosion resistant piping on the recirculating brine system to reduce the possibility of leaks;

- (4) The collection and recycle of all mercury contaminated floor washings;
- (5) Chemical treatment and settling of brine fed to the diaphragm cell plant for the removal of mercury.

At the present time, all of these procedures have been implemented. Average daily losses of mercury for the period May 15 to May 31 were 0.7 pounds per day.

Daily analytical checks of all plant effluents for mercury are carried out by the company and reports are submitted to the Ontario Water Resources Commission on a monthly basis. These reports are included in Appendix 1. At the same time, regular sampling and analysis is carried out by Ontario Water Resources Commission's personnel.

2.6 EFFECT OF MERCURY

(1) Concentrations in Fish

As discussed in Section 2.1, high concentrations of mercury were found in fish of various species in the St. Clair River - Lake St. Clair system. Further investigations revealed contaminated fish in Lake Huron, the Detroit River and Lake Erie. The mercury content of some fish was found to be as high as 7 ppm. A summary of the data collected from the analysis of fish is included in Appendix 2, Table 1.

(2) Concentrations in Water

Analysis for mercury were performed on water samples taken from Lake St. Clair and the St. Clair River on May 4, 1970. Mercury concentrations in all water samples except those in the immediate vicinity of the Dow outfalls were less than the detectable level of 0.005 mg/l. Samples immediately downstream of the outfalls contained up to 0.04 mg/l of mercury.

(3) Distribution in Sediments

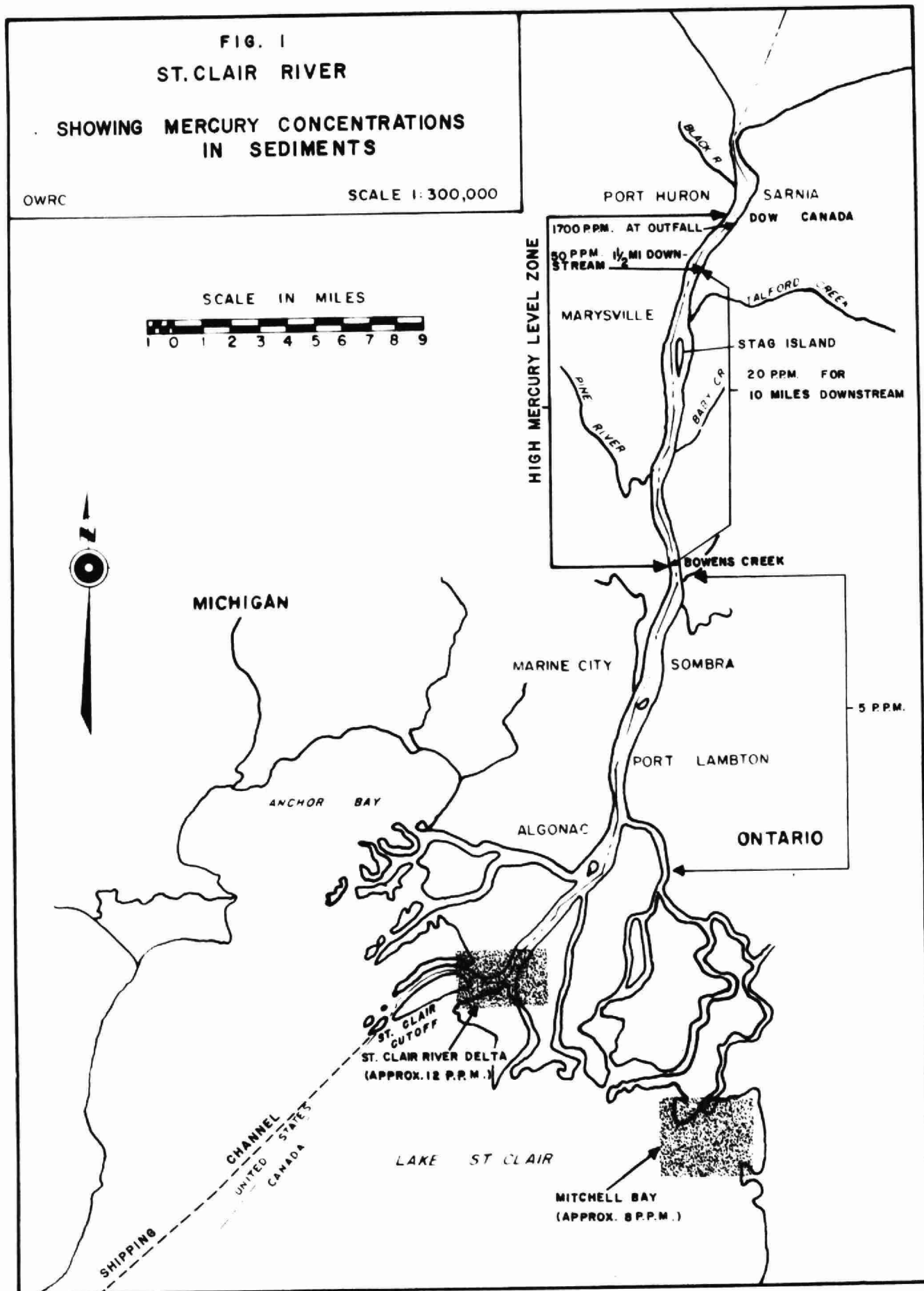
Mercury concentration in sediments as high as 1,700 ppm were found immediately below the Dow outfalls. Concentrations reduced to 50 ppm 1 1/2 miles downstream, and to 20 ppm ten miles further downstream. The areas with contaminated sediments are within 150 to 300 feet of the Canadian shore. This area is shown on

Figure 1 as the "high mercury level zone". The mercury concentrations in Lake St. Clair are generally less than 1 ppm showing gradation from the river inlet with pockets of mercury in the St. Clair River Delta and Mitchell Bay areas at levels of 12 and 8 ppm respectively. Some mercury has accumulated in the shipping channel in U. S. waters immediately below the St. Clair Cut-off Channel (a by-pass channel in the river delta area). It should be noted that the U. S. Corps of Engineers has requested advice from FWQA on disposal procedures for their channel maintenance dredging program this summer.

Concentrations of mercury in the sediments at the head of the Detroit River and in the outflow area of Lake St. Clair are in the order of 1 ppm.

Calculations based upon Dow's estimate of their mercury losses and the OWRC's estimate of the mercury distribution in the river sediments indicate that 20% of the total mercury losses from Dow are deposited in the bottom sediments in the 12 mile reach of the river immediately below the Dow plants.

A detailed description of the sediment sampling program appears in Appendix 2.



2.7 STATUS OF COMMERCIAL AND SPORT FISHERY

(1) Restrictions

The following restrictions were imposed on fishing in the Lake Huron - St. Clair River - Lake St. Clair - Detroit River - Lake Erie system:

March 24, 1970 - The Federal Government banned the sale and export of fish caught commercially within the Canadian boundaries of Lake St. Clair because a number of fish from these waters had been found to contain concentrations of mercury in excess of 0.5 ppm. Some fish contained as much as 7 ppm of mercury.

Ontario warned the public not to eat fish taken from Lake St. Clair and the St. Clair River.

March 30, 1970 - Catches of perch and pickerel from the Lake Erie commercial fishery were seized by Ontario.

April 3, 1970 - Most of the catches seized on March 30 were released when low levels of mercury in the fish were confirmed.

April 6, 1970 - Ontario announced a total ban on commercial and sport fishing on the St. Clair River, Lake St. Clair and the Detroit River. This closure affected approximately 70 licensed commercial fishermen.

April 8, 1970 - Michigan warned sportsmen not to eat fish taken from the St. Clair River, Lake St. Clair and the Detroit River.

April 10, 1970 - Michigan announced a total ban on commercial and sport fishing in the Michigan section of the St. Clair River, Lake St. Clair and the Detroit River.

April 13, 1970 - Ohio banned commercial fishing in Lake Erie.

April 30, 1970 - New York seized all fish caught commercially in the New York section of Lake Erie. New York advised fishermen against eating fish taken from Lake Erie. Ontario closed commercial fishing for white bass and pickerel in Lake Erie off the Counties of Kent, Essex and Elgin and commercial fishing for pickerel in Lake Huron off Lampton County. Michigan closed pickerel fishing in the Michigan section of Lake Erie.

May 14, 1970 - Ontario lifted the ban on sport fishing, but issued a strong recommendation against the consumption of fish taken. One week later, Michigan permitted sport fishing with no possession.

(2) Loans

The Ministers of the Ontario Department of Lands and Forests and the Canada Department of Fisheries and Forestry established a government committee to formulate a plan for making loans available to fishermen and other businesses directly affected by mercury pollution.

A formula was established which would enable commercial fishermen to borrow money on an interest-free demand note equivalent

to 70% of their 1969 gross revenue. The formula called for initial payments of 75% of the total approved loan with the remaining 25% being paid in the fall of 1970. On May 14, 27 cheques were issued.

There were an additional 15 applications from fishermen where there was some justification for not using 1969 gross revenues, i.e. purchase of new licences and equipment. These applications were referred back to the committee for individual consideration. As of June 4, 1970, the total money issued as loans to commercial fishermen amounted to \$100,545.

At this time, no formula has been developed for granting loans to bait dealers. The committee is waiting for substantiated claims before proceeding with the establishment of a formula. This matter will likely receive further attention in the near future.

A formula was originally developed for eight tourist camp operators who had requested loans. This formula would have provided money to cover 100% of fixed costs plus 70% of net profit. When the decision was made on the form of the Federal-Provincial agreement, the Federal Government would not agree to loans to camp operators and, for this reason, a new formula was determined essentially by the Ontario Cabinet which provided for 70% of gross revenues. However, as the Federal Government did not agree to their 50% portion, the Provincial Government made loans covering their 35% responsibility (i.e. 50% of 75% of the gross).

2.8 FUTURE COURSE OF ACTION AND ALTERNATIVES

Some of the possible solutions for reducing excess mercury residuals in Lake St. Clair and the St. Clair River are as follows:

- (1) Stop all discharges of mercury and take no further action other than permitting the system to gradually dissipate the mercury now present.
- (2) Convert mercury in the sediment into a form which is not available for aquatic life.
- (3) Cover the area contaminated by mercury with an impermeable membrane.
- (4) Remove the mercury contaminated sediment.

Some comments can be offered based on theoretical considerations and on experiments performed and reported in the literature.

(1) Take No Action

Mercury levels in most of the Lake St. Clair sediments are at such low concentrations that control over their effects is practically out of the question. Concentrating remedial efforts on the sections of the river in which mercury concentrations in sediments are the highest would, in the long term, probably hasten the overall recovery of the drainage system. Taking no action to reduce the effects of the mercury accumulations in the sediments of the St. Clair River system would prolong contamination of the sediments and fish and result in retardation of the overall recovery of the system. The following discussion

outlines the likely results of taking no action to correct the problem at this time.

Approximately 40,000 pounds of mercury are presently deposited in the bottom sediments within a limited area (12 miles long by 100 to 300 feet wide by 10 to 15 inches in depth) of the St. Clair River downstream from the Dow chlor-alkali complex. There is sufficient mercury in this area to cause high mercury concentrations in fish for many years to come.

If the metallic mercury is not removed from the system, it is probable that bio-chemical reaction would cause it to be converted to methyl mercury (as discussed in Section 2.2, Mercury as a Pollutant). It has been proposed by Jernelov (1969), that species of *Penicillium* can convert methyl mercury to dimethyl mercury, which has a low boiling point and could leave the water through volatilization. The net result could be the serious contamination of air, and the contamination of any water coming into contact with this air.

If the mercury is not removed, it could come into contact with sulfides occurring naturally in the river water. The sulfides could react with mercury to produce mercurous sulfide, an extremely insoluble compound. As mercurous sulfide, the mercury would not be available to the biota. However, all sulfides are prone to attack by both aerobic and anaerobic bacteria, and the very insoluble

sulfide could be converted to the stable, soluble sulfate readily available to the aquatic biota.

It should also be mentioned that vapours of mercury are readily absorbed through the respiratory system and while the vapour pressure of mercury is very low at ambient temperature, it is expected that mercury is always present in water that is in contact with mercury-containing sediment. Although concentrations in the water are low, this mercury might be readily taken up by fish and contribute to the accumulation of unacceptable concentrations in their flesh.

Construction dredging on the St. Clair River has shown that large quantities of sand and bottom sediments are continuously being carried along the river bottom as a bed load. This action alone could distribute the mercury now concentrated below Dow over large areas of Lake St. Clair and possibly even the Detroit River and Lake Erie.

While the water above the sediment contains undetectable concentrations of mercury, there is much evidence that considerable quantities of mercury could be fed into the food chain by bacteriological reactions. It appears obvious that the source for such future contamination must be removed or isolated from the water.

(2) Chemical Conversion of the Mercury

Mercury in various forms can be chemically converted into several very insoluble, stable compounds. By reacting it with an

excess of hydrogen sulfide or ferrous sulfide, mercury is transformed to mercurous sulphide which is virtually insoluble in water. By maintaining an excess of the sulfide, the mercury would be forced to remain as the sulfide.

The chemical conversion of metallic sulphide appears to be feasible only in a closed system. In a river bed, the conditions to keep the mercury in the sulfide form could not be maintained, and in time, the biological and bacteriological breakdown of the sulfide as mentioned above would free the mercury back to the food chain.

Some recent experiments have indicated that there is a possibility of fish picking up mercury in the sulphide form. If these experiments are substantiated, it may be found that no benefit would be derived by converting the mercury to mercurous sulphide.

Other insoluble mercury compounds, such as mercurous chloride and mercurous bromide could be formed, but both may revert to metallic mercury and the soluble toxic divalent mercury compounds in time, thereby negating a temporary relief.

Finally, it should be mentioned that the technical problems involved in having any chemical agent come into intimate contact with 40,000 pounds of mercury over such a large area and to such a depth (9-10 inches below the surface of the sediment) make the chemical conversion of the mercury impractical.

(3) Cover the Mercury-Laden Sediments

If the mercury-laden sediments could be covered in such a manner as to remove them from contact with the water and the biota, the net result would be equivalent to physically removing the mercury from the river. Any cover that would isolate the mercury from the water would have to possess the following qualities:

- (1) Scour resistant to prevent erosion by currents.
- (2) Impermeability to prevent any soluble mercury compounds formed in the sediments from entering the water.
- (3) Weight to prevent possible flotation by gases which could be produced by the decay of organic materials trapped under the cover.
- (4) Strength to resist physical damage from boats, anchors and possibly ice.
- (5) Resistance to chemical erosion to avoid eventual deterioration resulting in failure.

It is technically possible to design and construct such a cover, but the cost of the work would make this alternative impractical, especially since the possibility would exist of the cover material failing with the subsequent release of mercury sometime in the future.

(4) Remove Mercury Contaminated Sediments

Considerable mercury contamination of bottom sediments occur downstream from the Dow chlor-alkali plant in a section of the river, 12 miles long and approximately 150 feet wide, located adjacent to the Canadian shore. Results from preliminary sampling programs indicate that 9 to 12 inch depths of sediment are contaminated by the mercury.

From the Dow outfalls to downstream of the Sun Oil Company bottom sediments contain an estimated 15,000 pounds of mercury in a volume of 50,000 cubic yards. The section of the river from the Sun Oil Company to the south end of Stag Island contains an additional 15,000 pounds of mercury in a volume of 150,000 cubic yards of sediment. The remaining section of the river from Stag Island to 12 miles downstream of Dow contains approximately 10,000 pounds of mercury in a volume of 280,000 cubic yards of sediment.

For the 12 mile section of river located downstream from Dow, Figure 2 shows the percentage of mercury that could be removed from the river by dredging various percentages of the sediment located in the reach. Figure 2 shows a diminishing rate of return as the concentration of mercury declines.

Approximately 200,000 cubic yards (40% of the total sediment) appears to be the optimum amount of sediment to be removed. The

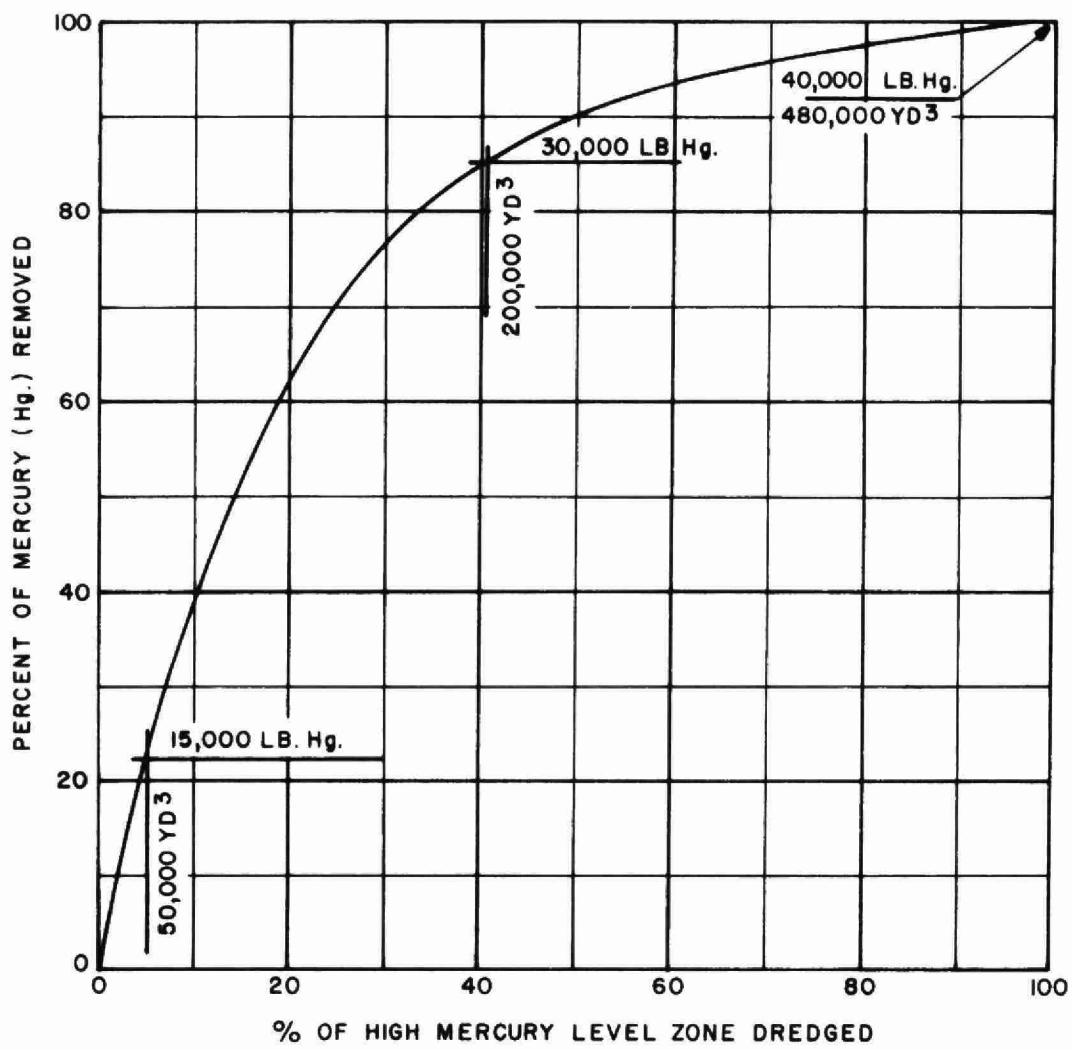
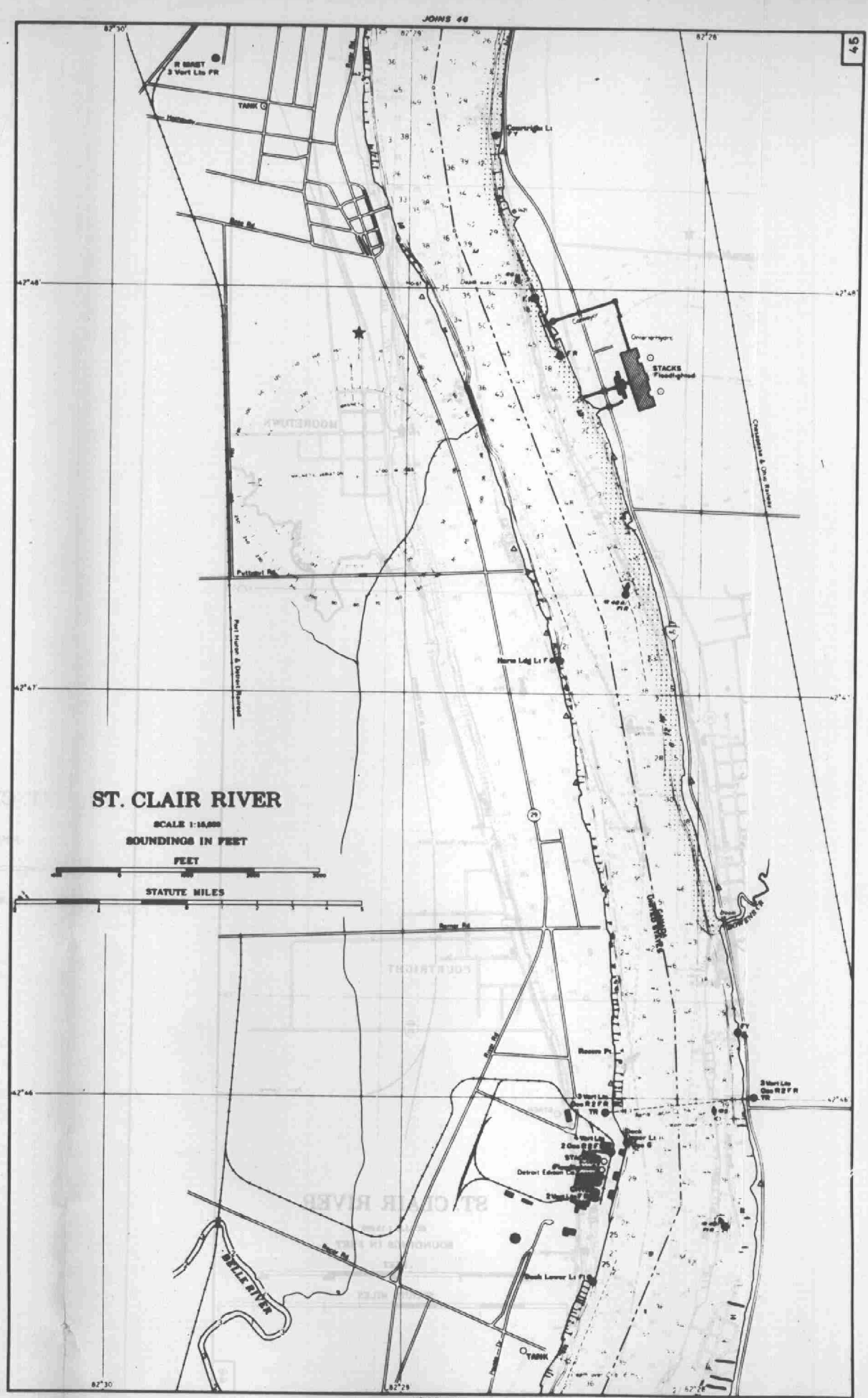
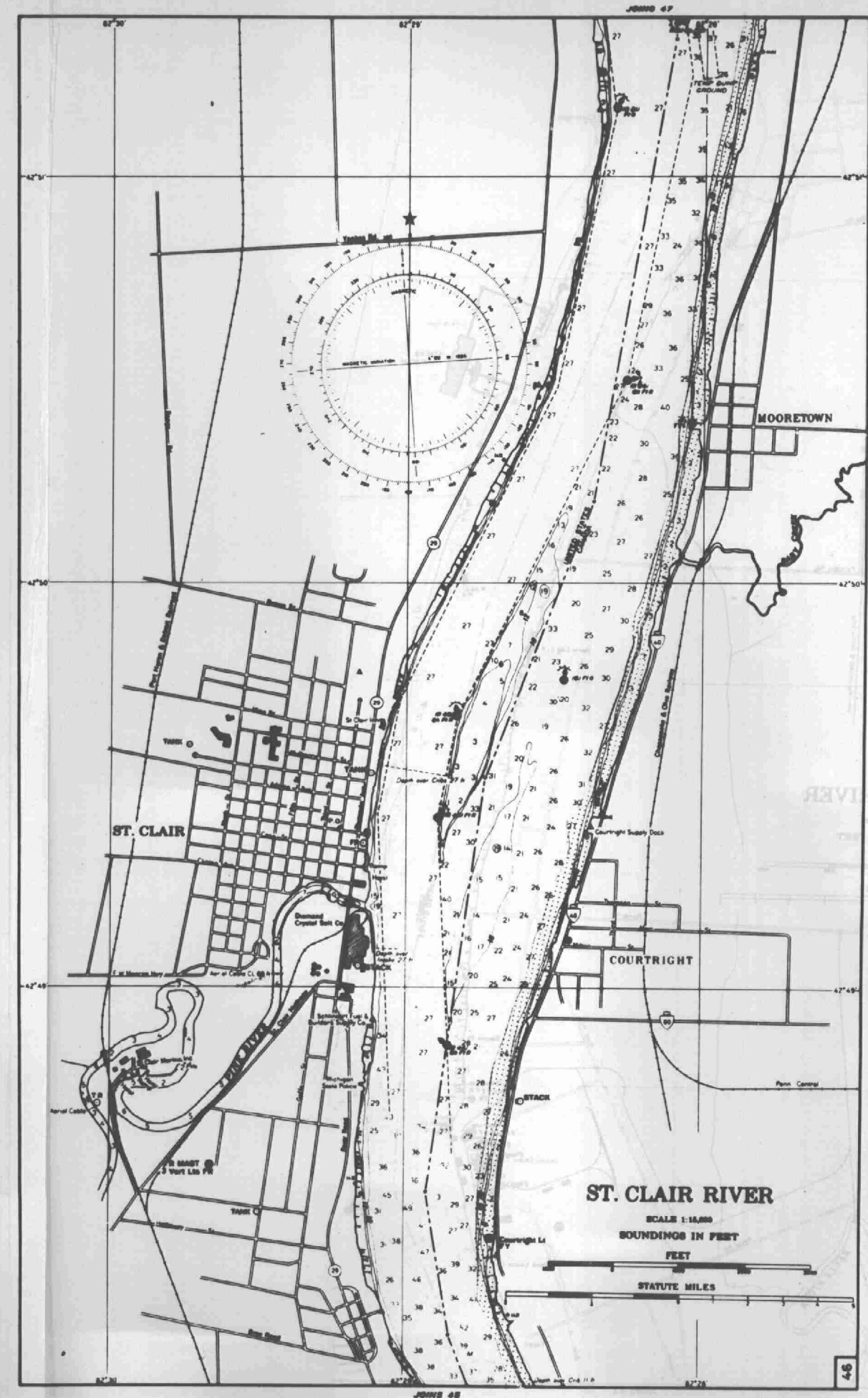
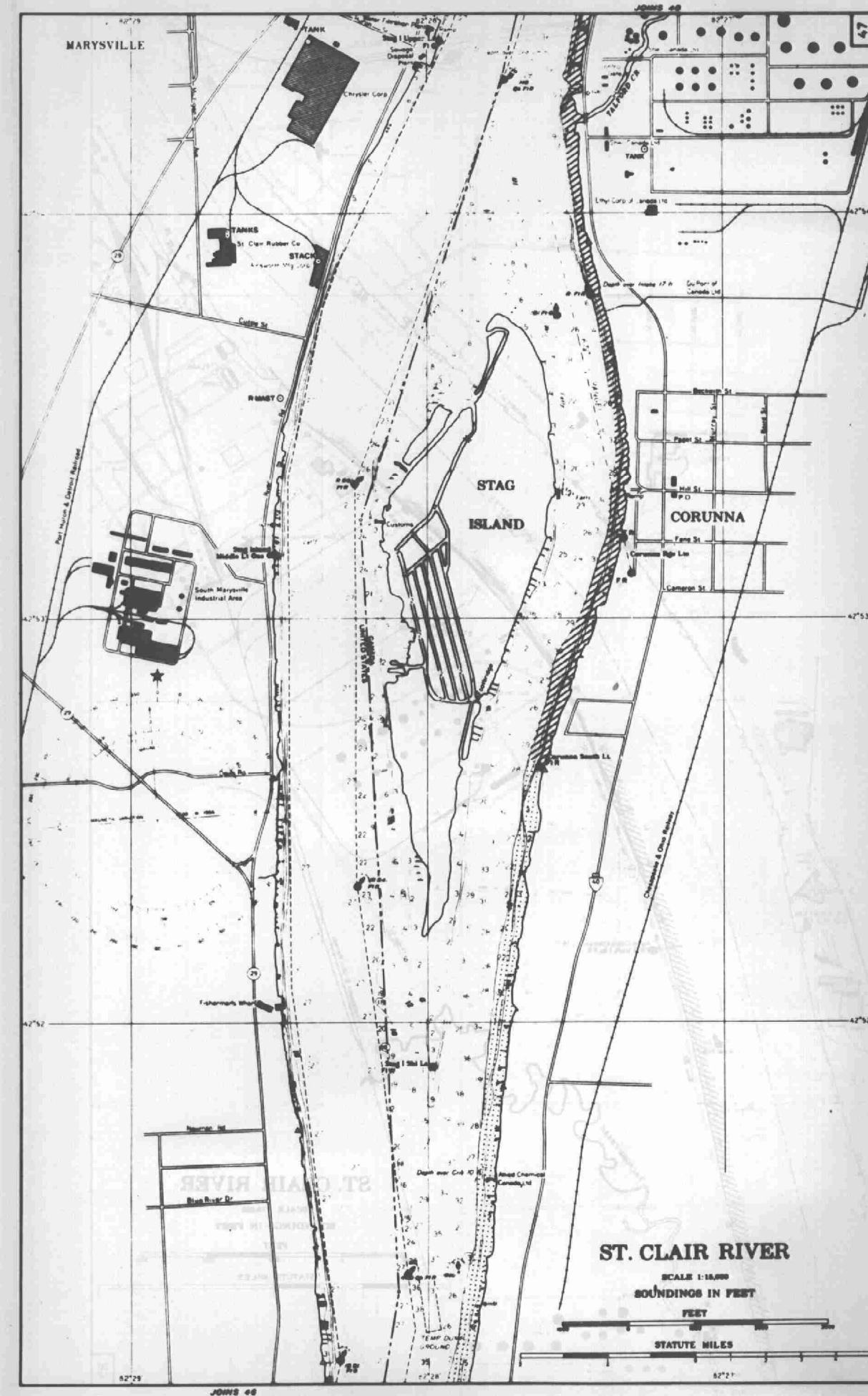


FIGURE 2
QUANTITATIVE RECOVERY OF MERCURY BY DREDGING SEDIMENTS
IN THE ST. CLAIR RIVER
BETWEEN DOW COMPLEX AND BOWENS CREEK

amount of mercury removal per cubic yard of sediment dredged in excess of 200,000 cubic yards is sufficiently low that dredging becomes impractical. Figure 3 indicates the areas of the river that would be affected by dredging 50,000, 200,000 and 480,000 cubic yards of sediment.

Experiments conducted by the OWRC indicate that the mercury contained in sediments will settle quickly after it is disturbed. If care is taken to minimize the disturbance of the sediments during dredging through the use of a modified suction dredge resembling those used in sand-sucking it should be possible to remove the mercury contaminated sediment with relatively little loss of mercury to the downstream section of the river. The mercury that becomes suspended in the water could be caught in a series of sediment traps cut into the riverbed downstream of the dredging operation. Sediment traps upstream of Lake St. Clair should be used to trap mercury that could be scoured with the river sediments. Regular cleaning or suitable sealing of these traps will eventually remove much of the mercury from the system that cannot be removed at this time by dredging.

A series of dredging experiments on the St. Clair River will be necessary in order to test techniques for large scale dredging of mercury contaminated sediments. These experiments would take into consideration possible damage to the downstream environment due to the loss of mercury in the vicinity of the dredge.



LEGEND

- APPROX. 50,000 YD³ CONTAINING 15,000 LB'S. OF MERCURY.
- APPROX. 150,000 YD³ CONTAINING 15,000 LB'S. OF MERCURY.
- APPROX. 280,000 YD³ CONTAINING 10,000 LB'S. OF MERCURY.

FIGURE 3
ST. CLAIR RIVER
ZONES OF HIGH MERCURY
CONCENTRATION

Investigations are presently underway to locate a suitable site for the disposal of mercury contaminated sediments. At this time, consideration is being given to the possible use of Stag Island, of Department of Highways land located along the river and of Dow property as disposal areas.

A properly designed lagoon would retain spoils without the risk of causing further damage to the environment. The lagoon could be built of clay and lined with a plastic material to make it totally impermeable. As the spoils are pumped into the lagoon, they could be treated chemically in order to render the mercury biologically inactive. When dredging is completed, the spoil area could be sealed off in order to prevent the loss of any mercury in the future.

Any disposal area will have to be capable of protecting the surrounding area from being damaged by the mercury contained in the sediment.

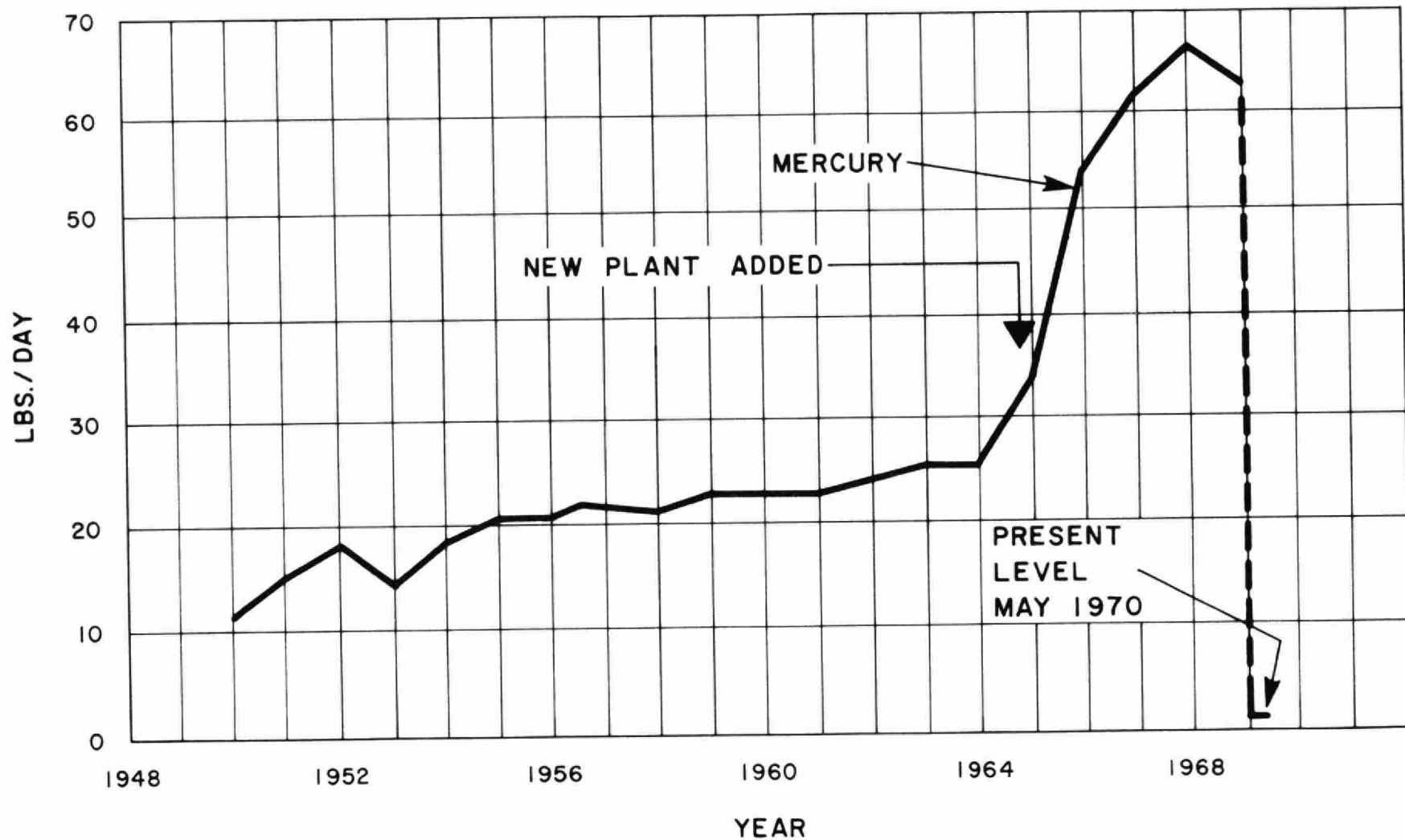
Other forms of dredging such as hopper and dipper dredging have been investigated but are not acceptable for removing mercury contaminated sediments. It is likely that dredging and associated spoil disposal will cost approximately \$3.00 per cubic yard.

Dredging appears to be the most suitable alternative available at this time. Even so, it must be recognized that it is not possible to dredge all mercury-laden sediments from the system. Dredging in

the most concentrated areas would accelerate the rate of recovery of the river and downstream lake areas.

APPENDIX I

MERCURY LOSSES TO
THE ST. CLAIR RIVER FROM
DOW CHEMICAL OF CANADA LIMITED
(SARNIA)



APPENDIX I - FIGURE 2

DOW (SARNIA) AVERAGE DAILY MERCURY LOSS TO SEWER BY YEAR



DOW CHEMICAL OF CANADA, LIMITED

SARNIA, ONTARIO

February 27, 1970

Mr. R. M. Gotts, P.Eng.,
District Engineer,
Division of Industrial Wastes,
O.W.R.C.,
135 St. Clair Avenue West,
Toronto 7, Ontario.

Dear Mr. Gotts:

This letter is written in reply to your letter of February 17, 1970 in which you requested:

- (a) A report on the action taken since the summer of 1969 to reduce mercury losses to the St. Clair River,
- (b) An outline in detail with anticipated scheduling of further work to eliminate mercury from our effluents,
- (c) An updating, every two weeks, of the progress made under (b),
- (d) An indication of the results that action already taken has had on mercury loadings.

I believe my letter of February 19, 1970 which you have since received covers items (a) and (b) above.

With regard to progress made on the scope of work identified in my letter, I would comment as follows:

Chlorine I - The piping up of the first 40 x 40 tank to accept brine from the closed brine recirculation system, when necessary, has been completed on schedule (February 25, 1970).

We expect today to complete the first phase of work to discontinue sending contaminated water from cell floor washings to the river, also as per schedule.

At this point in time we estimate that we are essentially on schedule with the other items at both Chlorine I and III for elimination of mercury to the river.

With regard to item (d) above, the following table summarizes the effect that action taken since last summer has had on mercury loadings.

Average Daily Losses - Lbs./Day

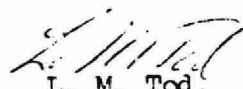
	<u>Chlorine I</u>	<u>Chlorine III</u>	<u>Total</u>
July 1969	45	140	195
August	45	110	155
September	110	70	180
October	*	40	*
November	45	10	55
December	68	40	118
January 1970	25	25	50
February	28	19	47

In October 1969, due to sewer repairs, we were prevented from obtaining samples of the Chlorine I effluent which was diverted through temporary piping discharging below the surface of the river.

The improvement trend in mercury loadings reflected in the above table is largely accounted for by the elimination of contaminated hydrogen spray cooling water to the effluent. Variations in mercury loadings in the effluents have mainly been due to periodic loss of brine from the closed brine recirculation system. Our program provides for the elimination of these losses through the measures identified to you, and which are partially completed at Chlorine I as mentioned above.

We trust the above information is that which you require at this point, and we will be pleased to assist you in any way we can opposite the solution of general problem of mercury losses in chlorine plants in the Province.

Yours very truly,


L. M. Todd,
Works Manager.

IMT/jah

	Chlorine I Effluent		Chlorine II Effluents		Chlorine III Effluent	
	Chlorine/Caustic/Seawater		Feed Brine	First St. Sluice	Domestic Alloy	
	PPM	#/Day	PPM	#/Day	PPM	#/Day
April 9	0.002	0.032	0.043	0.53	0.003	0.45
	*0.009	0.144			*0.030	1.20
April 10	0.007	0.112	0.032	0.38	0.012	1.80
	*0.014	0.224	0.033	0.40		
			0.028	0.34		
April 11	0.004	0.064	0.023	0.28	0.004	0.60
	*0.008	0.128	0.030	0.36	*0.009	0.36
			0.030	0.36		
April 12	0.010	0.160	0.087	1.0	0.005	0.75
	*0.011	0.176	0.110	1.31		
			0.090	1.10		
April 13	0.004	0.064	0.050	0.60	0.005	0.75
	*0.005	0.096	0.040	0.48	*0.005	0.20
			0.040	0.48		
April 14	0.002	0.032			0.012	1.80
	*0.005	0.096			*0.004	0.60

Samples: Samples are "spot" samples except as follows:

* Continuous 24 hour sample.

Flows: Estimated by Dilution Tracer Technique on April 9, 10, 11.

Chlorine I - 16 MM lb. per day.

Chlorine II - 150 MM lbs. per day

Chlorine III - 40 MM lbs. per day.

Chlorine II - Feed (Metered) - 12 MM lbs. per day.

Analysis: By Atomic Absorption Flameless Method.

Analysis of Effluents to the St. Clair River for Mercury

	Chlorine I Effluent		Chlorine II				Chlorine III Dominion Alloy	
	Chlorine/Cerclite South		Feed Brine		First Street Effluent		Effluent	
	PPM	#/Day	PPM	#/Day	PPM	#/Day	PPM	#/Day
April 30	0.005*	0.075	0.05 ^c	0.6	0.005 ^c	0.80	0.006 ^c	0.23
May 1	0.005*	0.075	0.04 ^c	0.48	0.006 ^c	0.96	0.006 ^c	0.23
May 2	0.006*	0.090	0.02 ^c	0.24	0.004*	0.64	0.008	0.30
May 3	0.001*	0.015	0.04 ^c	0.48	0.003*	0.48	0.005 ^c	0.23
May 4	0.001*	0.015	0.02 ^c	0.24	0.002 ^c	0.32	0.008 ^c	0.30
May 5	0.002*	0.030	0.03 ^c	0.96	0.005	0.80	0.005 ^c	0.19
May 6	0.003*	0.045	0.04 ^c	0.48	0.010*	1.60	0.005 ^c	0.19
May 7	0.001 ^c	0.015	0.08 ^c	0.96	0.002*	0.32	0.004 ^c	0.15
May 8	0.004*	0.064	0.06 ^c	0.72	0.004*	0.64	0.007 ^c	0.27
May 9	0.003*	0.045	0.06 ^c	0.72	0.004*	0.64	0.019 ^c	0.45
May 10	0.001*	0.015	0.10 ^c	1.20	0.002*	0.32	0.003 ^c	0.11
May 11	0.006*	0.096	0.10 ^c	1.20	0.004 ^c	0.64	0.004 ^c	0.15
May 12	0.002*	0.030	0.09 ^c	1.08	0.001*	0.16	0.004 ^c	0.15
May 13	0.003*	0.045			0.002*	0.32	0.013 ^c	0.50

Sampling: * Denotes continuous 24 samples.

^c Denotes lab composite of two samples taken per shift.

Analysis: Atomic Absorption Flameless method for total mercury.

Flows: Estimated by dilute tracer technique, as of April 15.

Chlorine I Effluent - 15 mm lbs./day
 II " - 160 mm lbs./day
 III " - 38 mm lbs./day
 Chlorine I Feed - 12 mm lbs./day/metered.

Analysis of Effluents to the St. Clair River for Mercury

	Chlorine I Effluent		Chlorine II				Chlorine III - Dormition Alley	
	Chlorine/Chloride South		Feed Brine		First Street Effluent		Effluent	
	PPM	#/Day	PPM	#/Day	PPM	#/Day	PPM	#/Day
May 13	0.003*	0.105	0.095 ^c	1.1	0.002*	0.32	0.013*	0.806
14	0.004*	0.140	0.11 ^c	1.32	0.004*	0.64	0.004 ^c	0.248
15	0.003*	0.105	-	-	0.003*	0.48	0.005 ^c	0.310
16	0.002*	0.070	0.077 ^c	0.92	0.001*	0.32	0.004*	0.248
17	0.004*	0.140	0.093 ^c	1.18	0.001*	0.32	0.006*	0.373
18	0.003*	0.105	0.102 ^c	1.22	0.002*	0.32	0.010*	0.621
19	0.002*	0.070	0.13 ^c	1.55	0.001*	0.16	0.012*	0.745
20	0.005*	0.175	0.12 ^c	1.44	0.005*	0.84	0.012*	0.745
21	0.014*	0.490	0.11 ^c	1.32	0.004*	0.64	0.020*	1.240
22	0.002*	0.070	0.048 ^c	0.58	0.001*	0.16	0.014*	0.870
23	0.005*	0.175	0.033 ^c	0.40	0.001*	0.16	0.021*	1.300
24	0.003*	0.105	-	-	0.001*	0.16	0.003*	0.186
25	0.002	0.070	0.077 ^c	0.92	0.001*	0.16	0.004*	0.248
26	0.013*	0.450	0.137 ^c	1.65	0.007	1.12	0.023*	1.430
27	0.001*	0.035	0.053 ^c	0.63	0.004*	0.64	0.005*	0.310
28	0.001*	0.035	0.033 ^c	0.40	0.001*	0.16	0.003*	0.186
29	0.001*	0.035	0.028 ^c	0.34	0.002*	0.32	0.005*	0.310
30	0.005*	0.175	0.023 ^c	0.27	0.002*	0.32	0.045*	0.310
31	0.001*	0.035	0.013 ^c	0.15	0.002*	0.32	0.002*	0.124
Average		0.136				0.37		0.56

Sampling - * Denotes continuous 24 hour samples.
- ^c Denotes lab composites of 2 samples taken per shift.

Analysis - Atomic Absorption Flameless method for total mercury.

Flows - Estimated by dilute tracer technique, as of May 13.
Chlorine I Effluent - 35 mm #/day
Chlorine II " - 160 mm #/day
Chlorine III " - 62 mm #/day
Chlorine I Feed - 12 mm #/day

Comments:

- (1) Total mercury discharges from Chlorine I, II and III for the period May 13 through May 31, 1970 approximates one pound per day.

APPENDIX 2

SUMMARY OF MERCURY ANALYSIS

FOR ST. CLAIR RIVER AND LAKE ST. CLAIR

APPENDIX 2

A description of the sediment sampling program is as follows:

(i) Lower Lake Huron

Sediment samples were taken on April 24, 1970 at four locations in Lake Huron approximately 3 miles north of the Blue-Water Bridge (see Appendix 2, Chart No. 1). The levels of mercury found at these four locations reflect a background concentration for this area of the lake and are not attributed to a specific source.

(ii) St. Clair River

Extensive sampling of sediments was carried out in the St. Clair River during the month of May, 1970, of nine samples taken upstream of Dow Chemical Co. property, only two showed a mercury concentration of greater than 1.0 ppm, i.e. 47.2 ppm and 2.1 ppm at 20 and 50 feet from shore immediately upstream of the Dow northern property boundary. A mercury concentration of 598 ppm was found downstream of the Dow "north chlorine caustic sewer" outfall, 1,700 ppm at a point 20 feet below the Dow "south chlorine caustic sewer" outfall and 329 ppm at 100 feet below the Dow "Dominion-Alloy sewer" outfall. The observed mercury content of the sediments offshore of

the Dow property and downstream to Stag Island is shown on charts No. 2 and 3 of Appendix 2. In general, suitable samples of the substrate for mercury determination were obtained only within 100 to 150 feet offshore. Beyond this, the substrate is either coarse gravel or very hard clay where the strong current precludes the possibility of fine materials settling out. It is not expected that significant accumulations of mercury exists on the river bottom beyond 150 feet from shore in this stretch of the river.

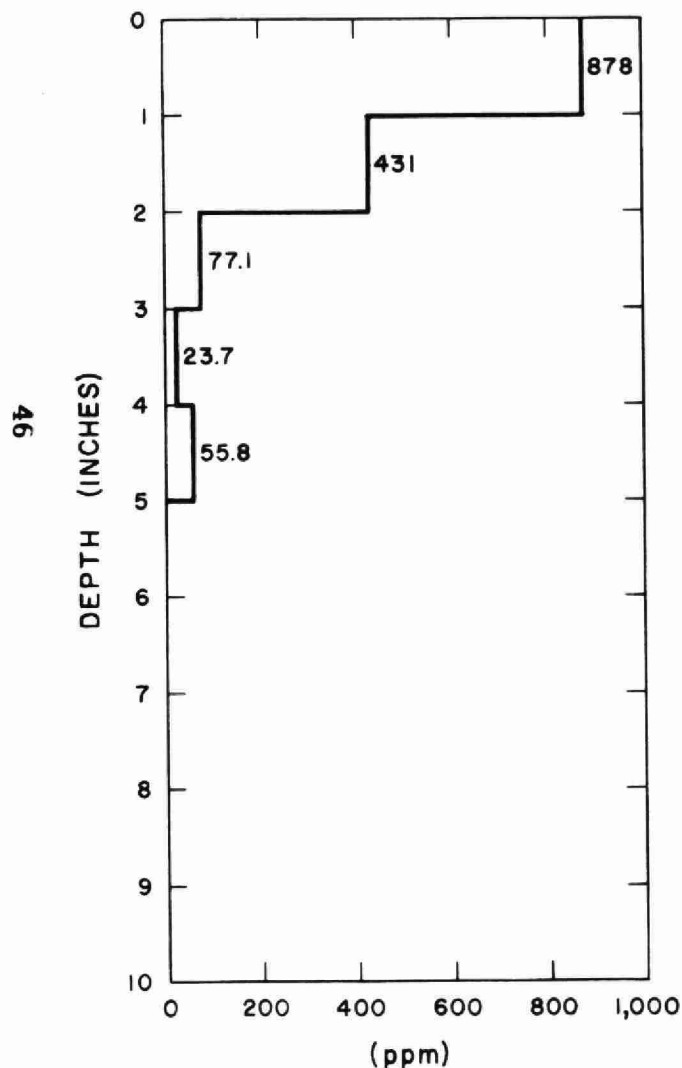
Below Stag Island, sediment samples varied widely in mercury content along the Canadian shoreline but very little mercury accumulation was noticed on the U. S. side as would be expected in view of the strong current. Some decrease in the mercury concentration in a downstream direction was observed.

(iii) St. Clair Delta and Lake St. Clair

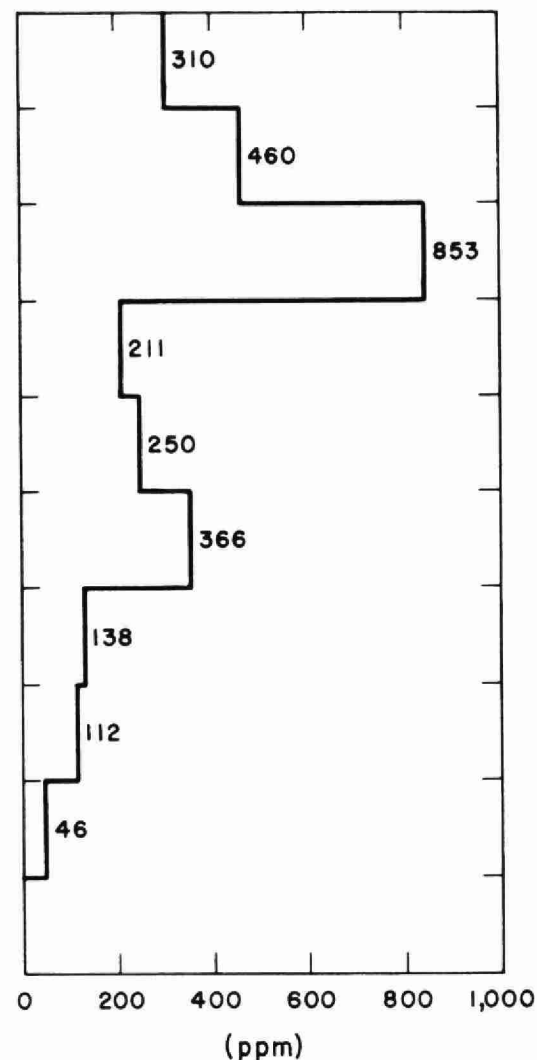
Deposition of mercury in Lake St. Clair in the vicinity of the discharge points of these channels is indicated on Chart No. 4 of Appendix 2, however, it is generally observed that mercury levels in the lake are somewhat less than those formed in the channels themselves. There is a definite gradation of mercury levels in the

sediments of Lake St. Clair being higher near the Delta
and decreasing toward the head of the Detroit River
where the observed level is less than 0.5 ppm.

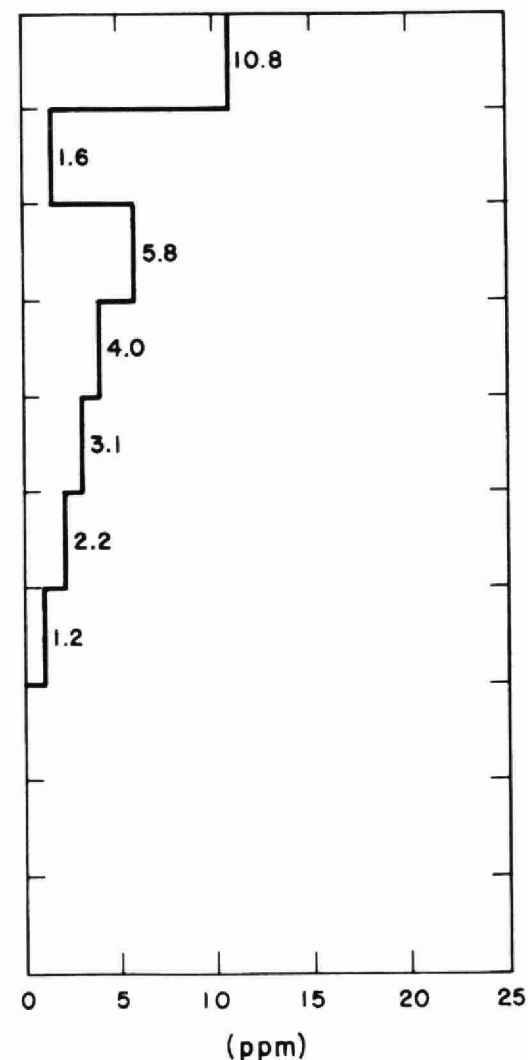
FIGURE 1 APPENDIX 2
MERCURY CONTENT IN SEDIMENT CORES TAKEN AT THREE LOCATIONS
IN THE VICINITY OF THE DOW (SARNIA) PLANT
(REPORTED IN ppm)



75 FT. BELOW CHLORINE
CAUSTIC NORTH SEWER
(15 FT. OFFSHORE)



100 FT. BELOW DOW
NORTH DOCK
(15 FT. OFFSHORE)



SOUTH END OF DOW
PROPERTY
(25 FT. OFFSHORE)

APPENDIX 2

TABLE 1

Summary of Mercury Analyses on fish collected from Southern Lake Huron, St. Clair River, Lake St. Clair, Detroit River and Lake Erie (Erieau to Detroit River). Results represent those available from FRB, OWRC, Gulf and U of T*laboratories as of first week of June, 1970.

Location	Species	Lab	No.	Min.	Max.	Mean
LAKE HURON						
South End	Pickerel	FRB	(3)	.18	2.23	1.36
		OWRC	(2)	1.20	1.50	1.35
		Gulf	(3)	.89	1.43	1.11
	Whitefish	FRB	(2)	.09	.10	.10
	Coho	"	(1)	-	-	.17
	Perch	"	(1)	-	-	.38
	Sucker	"	(1)	-	-	.52
	Rock bass	Gulf	(2)	.55	4.64	2.59
Port Franks	Pickerel	OWRC	(9)	.30	.96	.60
	Whitefish	"	(9)	.04	.67	.14
	Coho	"	(14)	.05	.13	.08
	Perch	"	(12)	.12	.34	.22
	Rock bass	"	(1)	-	-	.23
	White bass	"	(5)	.07	1.77	.93
	Sucker	"	(2)	.08	.11	.10
	Rainbow	"	(1)	-	-	.11
Grand Bend	Smelt	OWRC	(4)	.06	.07	.06
	Whitefish	FRB	(1)	-	-	.09
Bayfield	Coho	FRB	(1)	-	-	.18
Goderich	Coho	FRB	(1)	-	-	.22
ST. CLAIR RIVER						
	Pickerel	OWRC	(8)	.42	3.99	1.97
		Gulf	(3)	1.89	2.43	2.10

Location	Species	Lab	No.	Min.	Max.	Mean
ST. CLAIR RIVER (cont'd)	Pumpkinseed	OWRC	(2)	.34	.48	.41
		Gulf	(3)	.26	7.09	2.64
	Pike	OWRC	(1)	-	-	.90
		Gulf	(1)	-	-	1.04
	Coho	OWRC	(2)	.08	.09	.09
	Shad	"	(1)	-	-	.61
	Rock bass	Gulf	(3)	2.06	4.51	2.94
	Silver bass	"	(1)	-	-	1.62
	Small mouth bass	OWRC	(10)	1.1	5.2	2.61
	Walleye	OWRC	(2)	0.28	0.90	0.59
LAKE ST. CLAIR	Pickrel	FRB, Gulf	(16)	1.00	5.01	2.24
		U of T	(9)	.22	1.54	.54
		OWRC	(7)	.90	4.30	2.60
Thames River	Pike	FRB	(3)	.85	1.65	1.35
		U of T	(3)	.32	.63	.44
	Rock bass	FRB	(5)	1.49	5.44	3.14
	Black bass	FRB	(1)	-	-	4.12
	Silver bass	"	(3)	.54	2.92	1.60
	Sheepshead	"	(4)	.39	2.27	1.18
	Suckers **	"	(14)	.22	5.13	2.00
	Catfish	"	(3)	.17	2.18	1.00
	Sturgeon	"	(2)	1.04	3.44	2.24
	Muskellunge	"	(1)	-	-	1.98
	Coho	"	(1)	-	-	.11
	Mooneye	"	(1)	-	-	2.85
	Gizzard Shad	"	(1)	-	-	.89
DETROIT RIVER	Pike	OWRC	(12)	.12	.99	.77
		FRB	(1)	-	-	1.52
	Black bass	"	(1)	-	-	1.51
	White bass	OWRC	(1)	-	-	.18
	Gar	"	(1)	-	-	.10
	Carp	FRB	(1)	-	-	.74
		OWRC	(6)	0.10	1.7	.82
LAKE ERIE Western Basin	Perch	FRB	(34)	.09	1.01	.34
	Pickrel	"	(2)	.43	1.43	.93

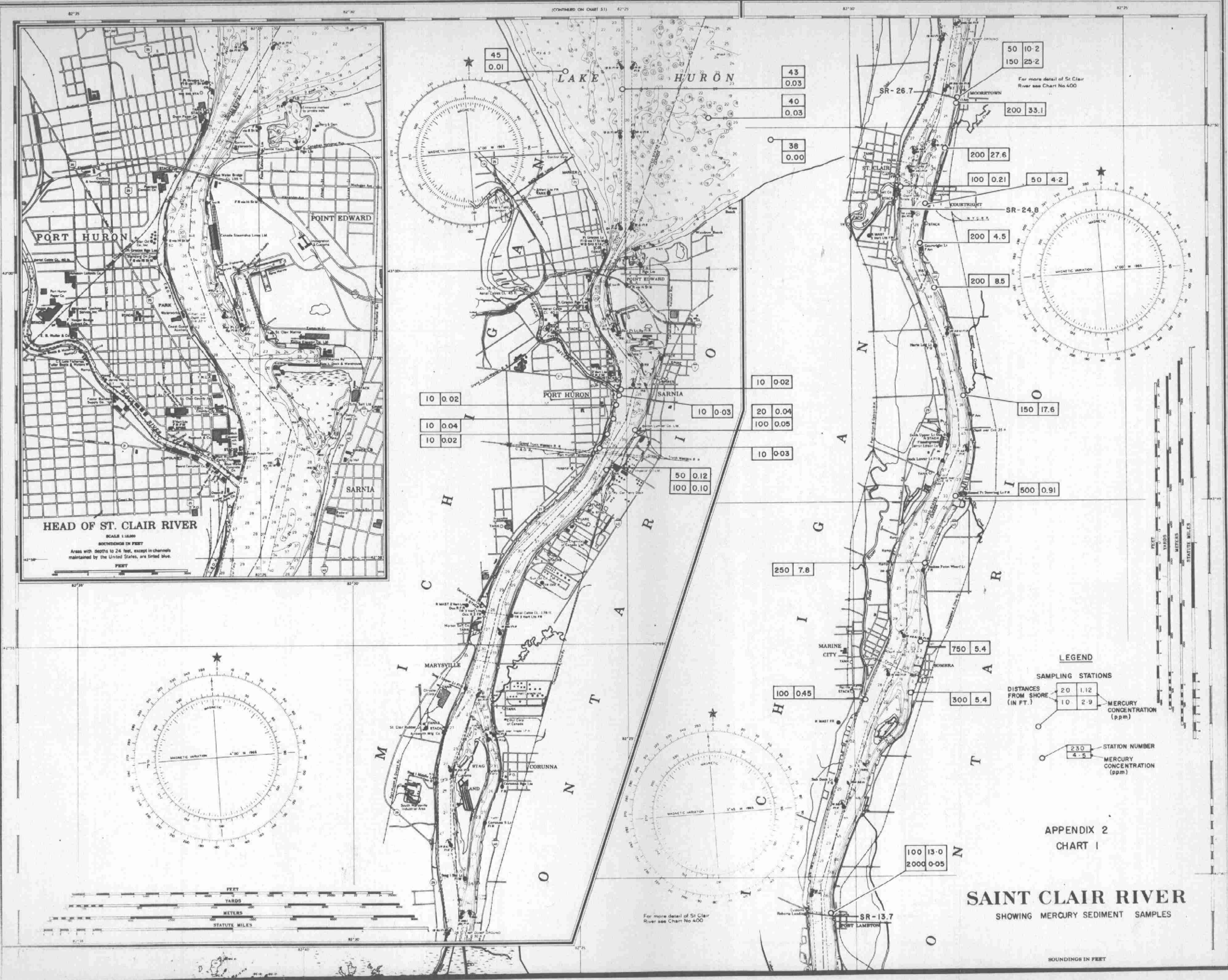
Location	Species	Lab	No.	Min.	Max.	Mean
LAKE ERIE (cont'd)						
	Pickereel	OWRC	(2)	.90	1.13	1.02
	Smelt	FRB	(2)	.06	.63	.35
	White bass	"	(4)	.74	1.09	.89
	Silver bass	"	(4)	.08	1.03	.54
	Catfish	"	(2)	.34	.40	.37
Erieau	Perch	FRB	(7)	.17	.35	.23
	White bass	"	(2)	.53	.60	.57
	Silver bass	OWRC	(9)	.14	1.71	.55

- * FRB - Fisheries Research Board Laboratory - Winnipeg
 OWRC - Ontario Water Resources Commission - Toronto
 U of T - University of Toronto Laboratory - Toronto
 Gulf - Gulf Atomic - California

** Includes "redfins", " mullet", common white and quillback suckers.

Note:

Questionable data were not included.



PORT HURON

POINT EDWARD

LAKE HURON

PORT HURON

SARNIA

SARNIA

MARYSVILLE

CORUNNA

MAINE CITY

ROMBERA

PORT LAMBTON

HEAD OF ST. CLAIR RIVER

SAINT CLAIR RIVER

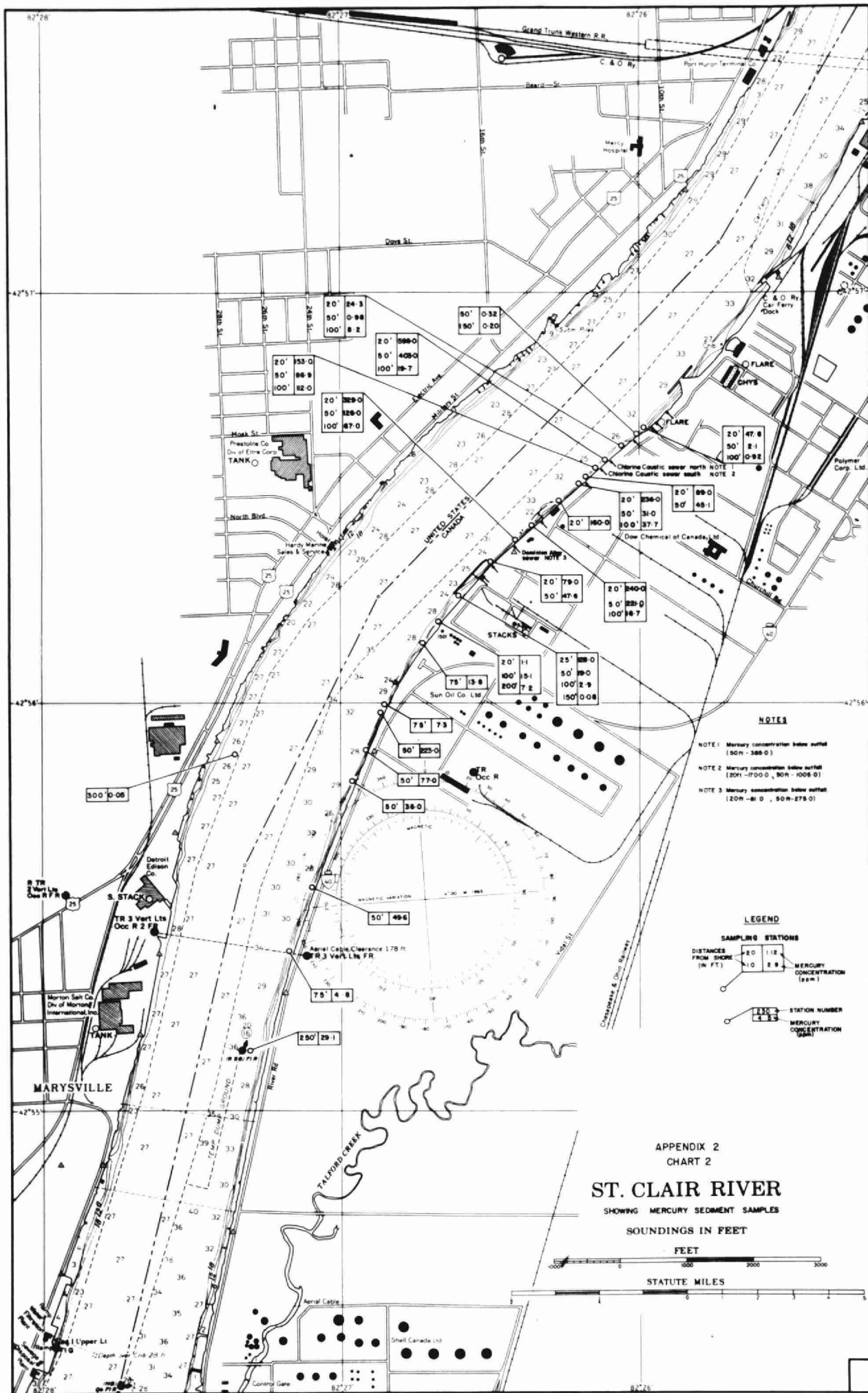
SHOWING MERCURY SEDIMENT SAMPLES

APPENDIX 2
CHART 1

LEGEND

- SAMPLING STATIONS
- DISTANCES FROM SHORE (IN FT.)
- MERCURY CONCENTRATION (ppm)
- STATION NUMBER
- MERCURY CONCENTRATION (ppm)

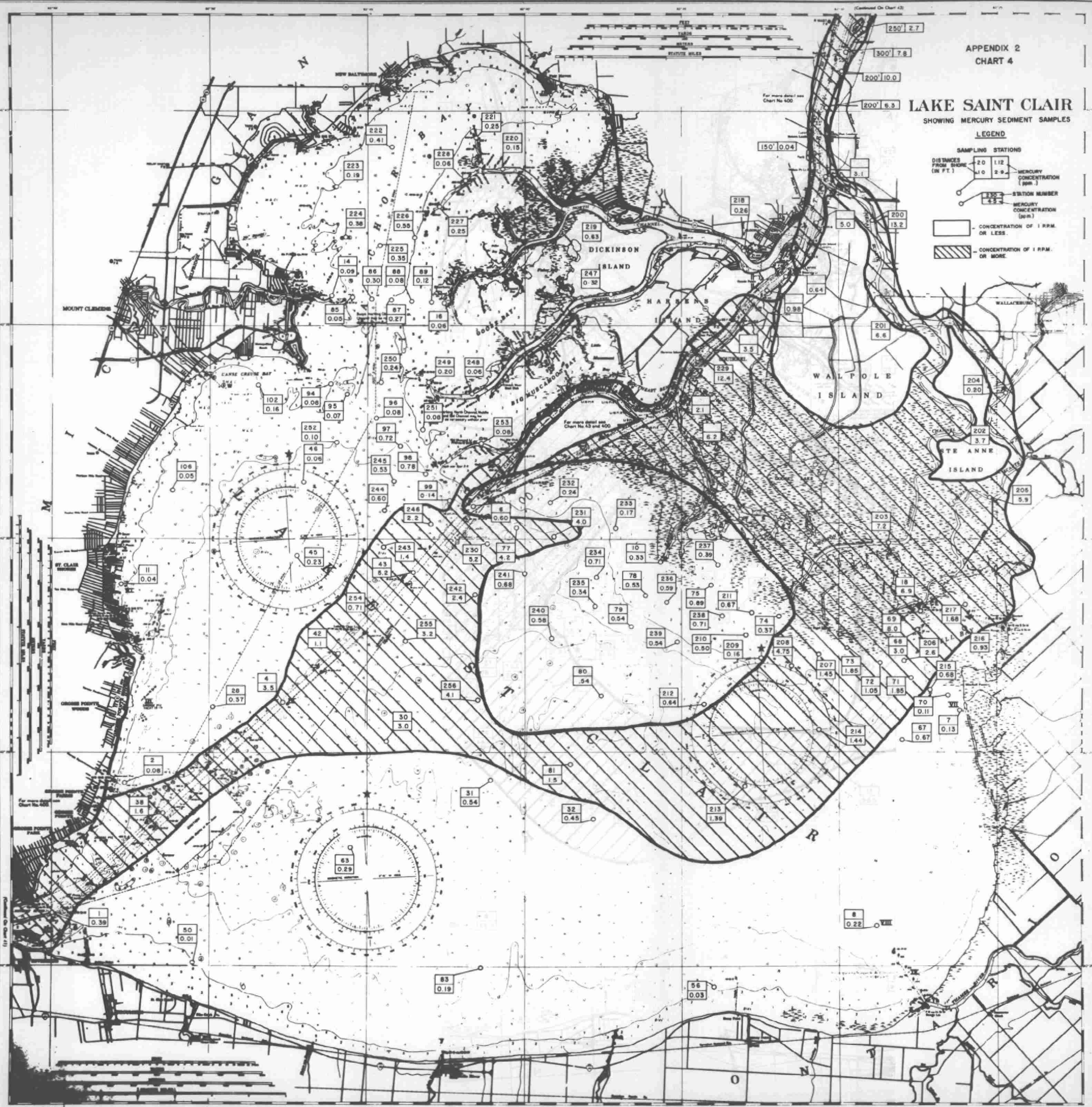
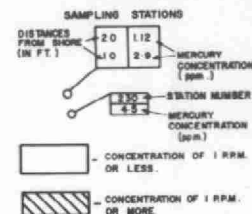
SOUNDINGS IN FEET



APPENDIX 2
CHART 4

LAKE SAINT CLAIR
SHOWING MERCURY SEDIMENT SAMPLES

LEGEND



APPENDIX 3

ANALYTICAL METHODS FOR MERCURY DETERMINATION

APPENDIX 3

ANALYTICAL METHODS FOR MERCURY DETERMINATION

In order to evaluate the effect of mercury on the aquatic environment, analyses of water, sediments, and biological material is required. The methods used for this analysis must be accurate, sensitive and quite rapid.

All of the methods require some form of sample preparation. This is necessary simply to obtain the mercury from the sample in a soluble form using oxidizing acidic solutions. This step is very time-consuming, especially in the case of sediments and tissue, due to the strength with which the mercury is bonded to the sample.

Several techniques may be used for the actual determination. The three most common are: neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS), and colorimetry. The NAA method, if carried out properly, is accurate and sensitive to low ppb ranges. However, the equipment is very expensive and this makes the NAA method prohibitive to most laboratories. The OWRC uses the AAS technique in routine work and the colorimetric method for control.

The AAS direct method is poor for mercury analysis, but the flameless AAS technique has been adapted and it is sensitive, accurate, and quite rapid (100 determinations daily). The determination can be performed in one of two methods, either by stripping the mercury from

the solution or by removing the air above the solution after equilibration of the mercury vapour takes place. The latter is the FRB method; the former is that used by Dow. OWRC labs have used both and prefer the mercury stripping method.

The classical dithizone colorimetric technique is more time-consuming and is used as a control, after the sample is further digested in a reflux system.

In summary, the OWRC regular method of analysis consists of a partial digestion followed by flameless AAS using the stripping technique. Intermittent controls are performed using a thorough digestion followed by dithizone extraction and measurement of the intensity of the colour.

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